

Synthesis, Crystal Structure and Theoretical Calculations of a Manganese(II) Coordination Polymer Assembled by 2,5-Thiophenedicarboxylic Acid and 3-(2-Pyridyl)pyrazole Ligands

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ABSTRACT A new Mn(II) complex, $[\text{Mn}_{0.5}(\text{tdc})_{0.5}(\text{L})]_{2n}$ (**1**, H_2tdc = 2,5-thiophenedicarboxylic acid, L = 3-(2-pyridyl)pyrazole), has been successfully synthesized under hydrothermal conditions. Its structure has been determined by single-crystal X-ray diffraction analysis, elemental analyses, IR, TG and UV spectrum. Single-crystal X-ray diffraction analysis reveals that complex **1** belongs to the orthorhombic system, space group $Pnna$ with $a = 11.5184(6)$, $b = 16.8399(8)$, $c = 11.7249(5)$ Å, $V = 2274.26(19)$ Å³, $Z = 4$, $D_c = 1.505$ g/cm³, $\mu = 0.715$ mm⁻¹, $M_r = 515.41$, $F(000) = 1052$, the final $R = 0.0336$ and $wR = 0.0802$ with $I > 2\sigma(I)$. It exhibits a one-dimensional zigzag-chain structure, which was stabilized through intermolecular C–H··O and intramolecular N–H··O hydrogen bonding interactions. Moreover, we analyzed Natural Bond Orbital (NBO) by using the PBE0/LANL2DZ method built in Gaussian 09 Program. The calculation results showed obvious covalent interaction between the coordinated atoms and Mn(II) ion.

Keywords: hydrothermal synthesis; crystal structure; Mn(II) complex; natural bond orbital;

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1 INTRODUCTION

Recently, studies on the synthesis of coordination polymers (CPs) have gained much concern in coordination chemistry owing to their interesting molecular topologies and enormous potential applications in catalysis, molecular selection, non-linear optics, ion exchange and microelectronics^[1-3]. In usual, the structural diversity of such crystalline materials depending on many factors, firstly, counteranion, templating agents, metal ion, metal-ligand ratio, pH value, and number of coordination situation given by organic ligands^[4-5]. In the specific

strategy, the sound selection of organic ligands or coligands in the light of their length, rigidity, and functional groups is important for the assembly of structural controllable CPs, and a lot of significant jobs have been done by using the tactics^[6]. Usually, the organic ligands with bent backbones, such as V-shaped, triangular, quadrangular, and so on, are great candidates for building highly high-connected, interpenetrating, or helical coordination architecture due to their bent backbones and versatile bridging fashions^[7, 8]. Moreover, the carboxylate groups are good hydrogen-bond acceptor as well as donor, depending on the degree of deprotonation. Among them, quadrangular polycarboxylic acids, such as 1,2,4,5-benzenetetracarboxylic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 4,4'-oxydibenzoic acid and 2,5-thiophene-dicarboxylic acid, are paid much attention owing to their rich coordination modes^[9]. Apart from the carboxylate linkers, chelating containing N-donor ligand, such as 1,10-phenanthroline, 2,2'-bipyridine, 3-(2-pyridyl)pyrazole, are frequently used in the assembly process of CPs^[10].

Hence, these considerations encouraged us to investigate new coordination frameworks with 2,5-thiophenedicarboxylic acid (H_2tdc) and containing N-donor ligand (L). Here, we report the synthesis and characteristics of a new CP, namely, $[Mn_{0.5}(tdc)_{0.5}(L)]_{2n}$ (**1**), which exhibits a one-dimensional *zigzag*-chain structure and is diverse from those of 2,5-thiophene-dicarboxylate-bridged complexes reported previously^[9(c)].

2 EXPERIMENTAL

2.1 General procedures

All the chemicals were purchased commercially and used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectrum was recorded in the range of 4000~400 cm^{-1} on a Nicolet 6700 Spectrophotometer using a KBr pellet. TG studies were carried out on a STA7300 analyzer under nitrogen at a heating rate of 10 $^{\circ}C\ min^{-1}$. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ range of 5~50 $^{\circ}$ with a scan speed of 0.1 $^{\circ}S^{-1}$ on a Bruker D8 Advance instrument using a $CuK\alpha$ radiation ($\lambda = 1.54056\ \text{\AA}$) at room temperature. UV spectrum was obtained on a Shimzu UV-250 spectrometer in the 200~400 nm range.

2.2 Synthesis of $[Mn_{0.5}(tdc)_{0.5}(L)]_{2n}$ (**1**)

A mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.05 g, 0.2 mmol), H_2tdc (0.068 g, 0.4 mmol), and L (0.029 g, 0.2 mmol) was dissolved in 18 mL H_2O . The final mixture was placed in a Parr Teflon-lined stainless-steel vessel (30 mL) under autogenous pressure and heated at 150 $^{\circ}C$ for five days, obtaining block crystals. The yield of the reaction was ca. 42%. Calcd. for $C_{22}H_{16}MnN_6O_4S$: C, 51.27; H, 3.13; N, 16.31%. Found: C, 50.01; H, 2.85; N, 16.03%. IR (cm^{-1}): 3113(w), 3023(w), 1944(w), 1604(s), 1582(m), 1533(m), 1432(m), 1360(s), 1306(w), 1250(w), 1229(m), 1154(w), 1114(w), 1111(w), 1094(w), 1065(w), 1015(w), 963(m), 899(w), 839(w), 792(s), 766(s), 709(w), 698(w), 682(w), 633(w), 593(w), 486(m), 469(w).

2.3 X-ray crystallography

All diffraction data of complex **1** were collected on a Bruker/Siemens Smart Apex II CCD diffractometer with

graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 293(2) K. Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares technique using the SHELXL-97 crystallographic software package^[11, 12]. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. For **1**, a total of 2818 reflections were collected in the range of $3.74 \leq \theta \leq 28.38^\circ$, of which 2368 were independent ($R_{\text{int}} = 0.0306$). The final $R = 0.0295$ and $wR = 0.1030$ for the observed reflections with $I > 2\sigma(I)$, and $R = 0.0336$ and $wR = 0.0802$ for all data with $(\Delta\rho)_{\text{max}} = 0.289$ and $(\Delta\rho)_{\text{min}} = -0.332$ e Å⁻³. Selected bond lengths and bond angles of complex **1** are shown in Table 1. Hydrogen bonding geometry for the title complex is collected in Table 2.

2.4 Theoretical calculation determination of complex 1

All calculations in this work were put into effect with the Gaussian09 program^[13]. The parameters of the molecular structure for calculation were all from the experimental data of the complex. Natural bond orbital (NBO) analysis was acted by density functional theory (DFT)^[14] with the PBE0^[15] hybrid functional and the LANL2DZ basis set^[16].

3 RESULTS AND DISCUSSION

3.1 IR spectrum

IR spectrum of **1** shows a broad absorption band at 3023 cm⁻¹ corresponding to the C–H stretching. Asymmetric and symmetric COO⁻ stretching modes of the lattice tdc²⁻ anion were evidenced by very strong, slightly broadened bands at 1604 and 1360 cm⁻¹^[17], which is consistent with the results of X-ray analysis.

3.2 Structure description

A single-crystal X-ray diffraction work displays that complex **1** crystallizes in the orthorhombic space group *Pnna* and shows a one-dimensional zigzag-chain structure. The coordination environment of Mn(II) in **1** is shown in Fig. 1. There are half Mn(II) ion, half tdc ligand and one L ligand in the asymmetric unit. The Mn(1) ion is six-coordinated by two carboxylate oxygen atoms (O(1), O(1A)) from two different tdc ligands and four nitrogen donors (N(2), N(2A), N(3), N(3A)) from two L molecules to provide a distorted octahedral coordination architecture. The bond distances of Mn–O in compound **1** are 2.1322(12) Å, and the Mn–N bond lengths fall in the 2.1915(14)~2.4086(15) Å range, which are in the normal range and the coordination angles around Mn atom vary from 70.43(5) to 166.75(5)°^[18]. In the coordination environment, the one carboxylate oxygen atom (O(1)) and three nitrogen atoms (N(2), N(2A), N(3)) are lied in the basal plane, while one carboxylate oxygen atom (O(1A)) and nitrogen atom (N(3A)) occupy the axial positions from the opposite direction. One coordination mode of the tdc ligand is present in the structure of complex **1**, namely a monodentate bridging mode. The L ligand exhibits a chelating mode, based on which two Mn(II) ions are linked by tdc ligands to produce a one-dimensional zigzag chain, which is different from those of 2,5-thiophenedicarboxylate-bridged complexes previously^[9(c)]. The distance

of neighboring Mn(II) ions is about 11.331 Å, as illustrated in Fig. 2. The L ligands locate in the chain up and down.

Hydrogen bonding interactions are frequently important in the synthesis of supramolecular framework. There are persistent intermolecular C–H··O and intramolecular N–H··N hydrogen bonding interactions between carboxylate oxygen atoms of tdc ligands, nitrogen atoms and carbon atoms of L ligands in complex **1** (Table 2). Thus, through hydrogen bonds, the one-dimensional *zigzag*-chains are further expanded into a three-dimensional supramolecular architecture (Fig. 3) and take an important effect in stabilizing complex **1**.

3.3 Powder X-ray diffraction (PXRD) and thermal stability

To confirm the phase purity of complex **1**, powder X-ray diffraction (PXRD) patterns were recorded for **1**, and it was comparable to the corresponding simulated patterns calculated from single-crystal diffraction data (Fig. 4), indicating a pure phase of bulky sample.

TG curve of **1** (Fig. 5) exhibits that the first weight loss of 34.2% from 317 to 400 °C corresponds to the removal of tdc ligand (calcd: 33.0%). Upon further heating, an clear weight loss (54.8%) occurs in the temperature range of 400~710 °C, corresponding to the release of L ligand (calcd: 56.3%). After 710 °C no weight loss is watched, which indicates the complete decomposition of **1**, the residual weight should be MnO.

3.4 UV spectrum analysis

The UV spectra for complex **1**, H₂tdc and L ligands have been discussed in the solid state. H₂tdc has one absorption band at about 273 nm and L has one absorption band at about 280 nm, whereas the title complex **1** has one absorption band at about 281 nm (Fig. 6), which should be assigned to the $n \rightarrow \pi^*$ transition of ligands and the charge transfer transition^[19].

4 THEORETICAL CALCULATIONS

The selected natural atomic charges and natural electron configuration for the complex are displayed in Table 3. It is shown that the electronic configurations of Mn(II) ion, N and O atoms are $4s^{0.22}3d^{5.51}4p^{0.39}$, $2s^{1.32-1.33}2p^{4.12-4.13}$ and $2s^{1.65}2p^{5.03}$, respectively. On account of the above results, one can infer that the Mn(II) ion coordination with N and O atoms is mainly on the $3d$, $4s$, and $4p$ orbitals. N atoms form coordination bonds with Mn(II) ion using $2s$ and $2p$ orbitals. All O atoms provide electrons of $2s$ and $2p$ to the Mn(II) ion and form the coordination bonds. Thus, the Mn(II) ion obtained some electrons from four N atoms of L and two O atoms of tdc^[16(a)]. Therefore, on the basis of valence-bond theory, the atomic net charge distribution and NBO bond orders of **1** (Table 3) indicate obvious covalent interaction between the coordinated atoms and Mn(II) ion. The differences of NBO bond orders

for Mn–O and Mn–N bonds make their bond lengths different^[16(b)], which is in good agreement with the X-ray crystal structural data of compound **1**.

As can be seen from Fig. 7, the lowest unoccupied molecular orbital (LUMO) mainly consists of L ligand, whereas the highest occupied molecular orbital (HOMO) is mainly composed of metal center. Thus, the charge transfer from metal to ligand may be deduced from some contours of molecular orbital of complex **1**.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn(1)–O(1)	2.1322(12)	Mn(1)–O(1A)	2.1322(12)	Mn(1)–N(2)	2.1915(14)
Mn(1)–N(2A)	2.1915(14)	Mn(1)–N(3)	2.4086(15)	Mn(1)–N(3A)	2.4086(15)

Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Mn(1)–O(1A)	95.55(7)	O(1)–Mn(1)–N(2)	101.92(5)	N(2A)–Mn(1)–N(3A)	70.43(5)
O(1A)–Mn(1)–N(2)	97.73(5)	N(2)–Mn(1)–N(3A)	166.75(5)	O(1)–Mn(1)–N(2A)	97.73(5)
O(1A)–Mn(1)–N(2A)	101.92(5)	N(2)–Mn(1)–N(2A)	150.61(8)	O(1A)–Mn(1)–N(3)	166.75(5)
O(1)–Mn(1)–N(3A)	166.75(5)	O(1A)–Mn(1)–N(3A)	92.81(5)	N(2A)–Mn(1)–N(3)	87.08(5)

Symmetry transformations used to generate the equivalent atoms: A: $-x, -y, -z$

Table 2. Hydrogen Bonds for Complex 1

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry codes
N(1)–H(1A)···O(2) ^{#1}	0.97(2)	1.67(2)	2.606(2)	160(2)	$x, 1/2-y, 1/2-z$
C(2)–H(2)···O(1) ^{#2}	0.93	2.50	3.425(2)	176	$1/2+x, -y, 1-z$

Table 3. Natural Atomic Charges, Natural Valence Electron Configurations, Wiberg Bond Indexes and NBO Bond Orders (a.u) for 1

Atom	Net charge	Electron configuration	Bond	Wiberg bond index	NBO bond order
Mn(1)	0.86024	[core]4s(0.22)3d(5.51)4p(0.39)			
O(1)	−0.69163	[core]2s(1.65)2p(5.03)	Mn(1)–O(1)	0.3887	0.3687
O(1A)	−0.69170	[core]2s(1.65)2p(5.03)	Mn(1)–O(1A)	0.3885	0.3687
N(2)	−0.29362	[core]2s(1.33)2p(3.93)	Mn(1)–N(2)	0.3299	0.3609
N(2A)	−0.29359	[core]2s(1.33)2p(3.93)	Mn(1)–N(2A)	0.3300	0.3609
N(3)	−0.45158	[core]2s(1.32)2p(4.11)	Mn(1)–N(3)	0.2673	0.2882
N(3A)	−0.45156	[core]2s(1.32)2p(4.11)	Mn(1)–N(3A)	0.2675	0.2882

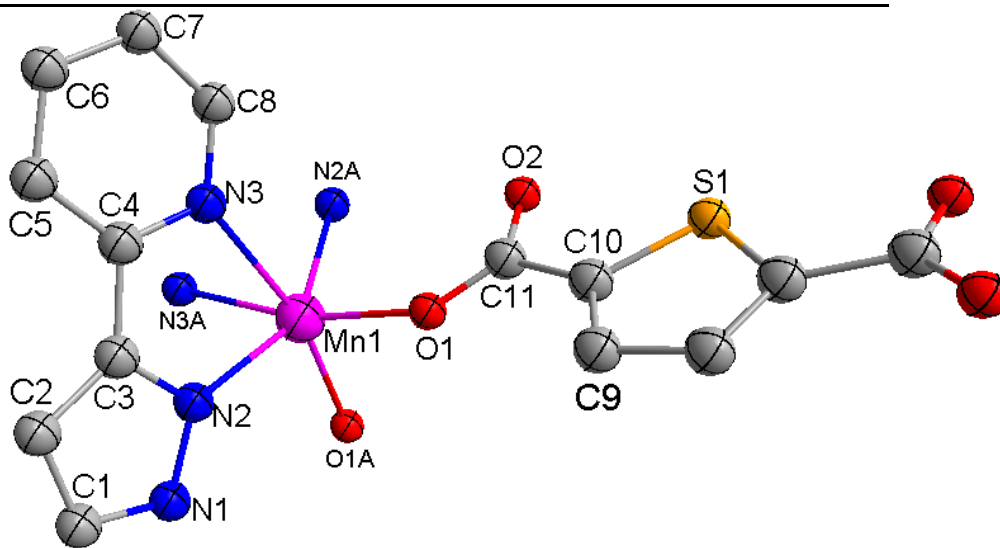


Fig. 1. Coordination environment of the Mn(II) center in 1. Symmetry code: (A) $-x, -y, -z$

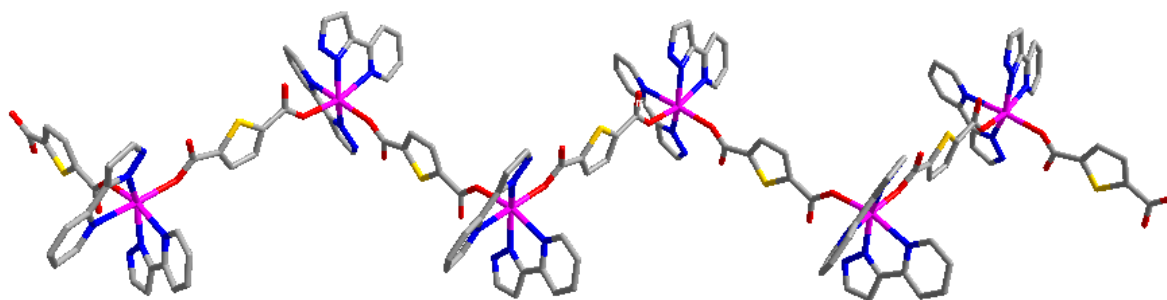


Fig. 2. View of the one-dimensional *zigzag* chain

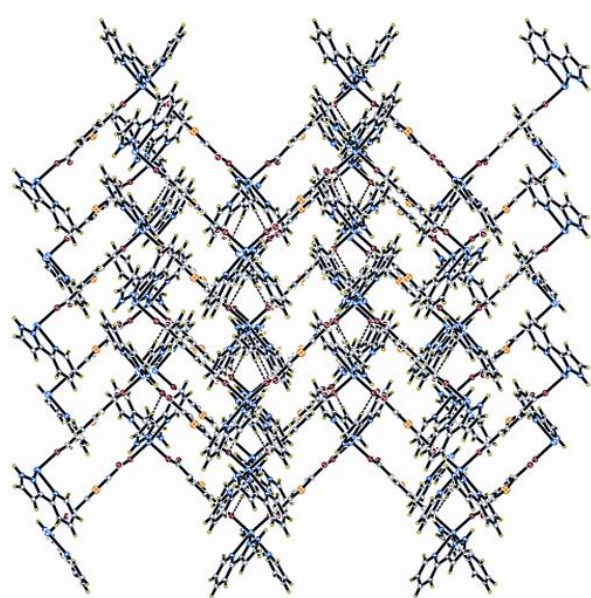


Fig. 3. View of the 3D supramolecular architecture of 1 formed by hydrogen-bonding interactions

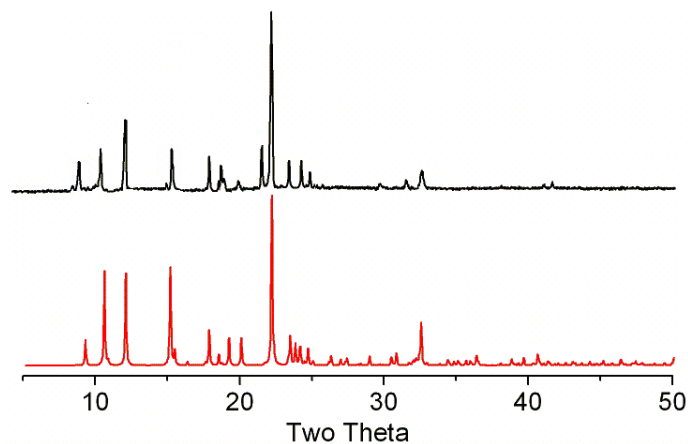


Fig. 4. PXRD analysis of the title complex: bottom-simulated, top-experimental

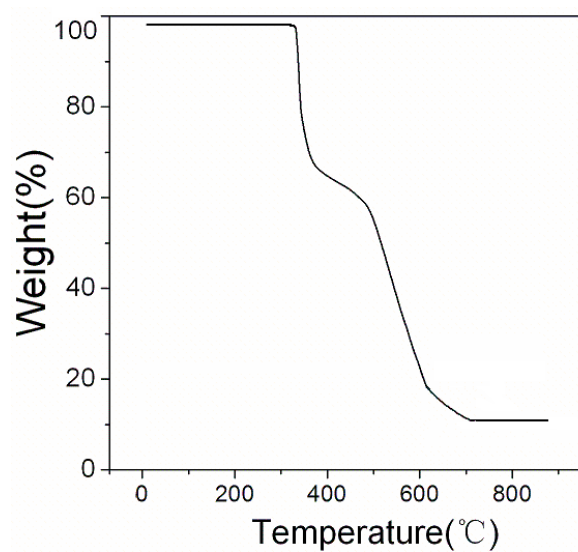


Fig. 5. TGA curve of complex 1

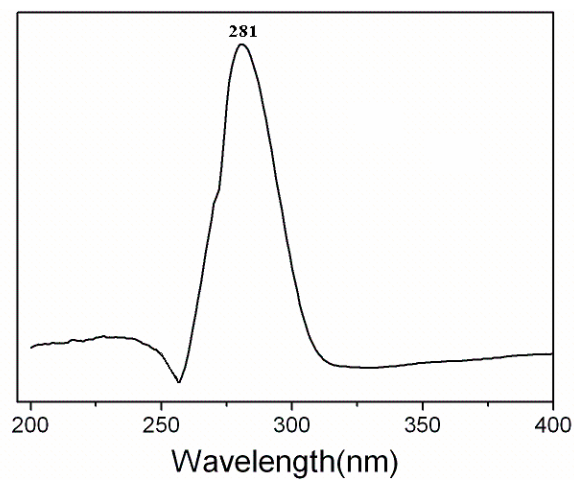


Fig. 6. UV spectrum of 1 at room temperature

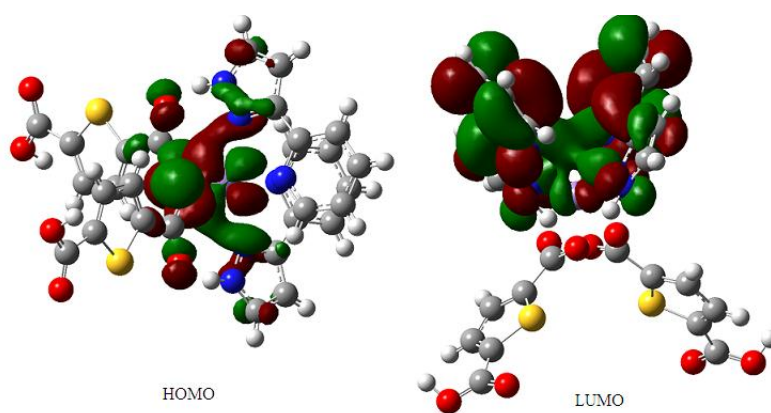


Fig. 7. Frontier molecular orbitals of complex 1

Synthesis, Crystal Structure and Theoretical Calculations of a Manganese(II) Coordination Polymer Assembled by 2,5-Thiophenedicarboxylic Acid and 3-(2-Pyridyl)pyrazole Ligands

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A new complex $[\text{Mn}_{0.5}(\text{tdc})_{0.5}(\text{L})]_{2n}$ has been successfully synthesized under hydrothermal conditions and its structure was determined by single-crystal X-ray diffraction analysis, elemental analyses, IR, TG and UV spectrum. **1** exhibits a one-dimensional *zigzag*-chain structure, which was stabilized through intermolecular C–H \cdots O and intramolecular N–H \cdots O hydrogen bonding interactions. Moreover, we analyzed Natural Bond Orbital (NBO) in using the PBE0/LANL2DZ method built in Gaussian 09 Program. The calculation results showed obvious covalent interaction between the coordinated atoms and Mn(II) ion.

